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## 45. Periodic Properties of Elements

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The periodic system of elements has been to the chemists a most important guiding principle in all speculations upon physical and chemical properties. Since its discovery it has been familiar to chemists that a recurrence of the properties appears in all the periods in like order, but of different degree, while the elements in the same family exhibit closely resembling properties which vary with atomic number in some more or less gradual manner. The periodicity is shown by the theory of atomic structure to be due to the outer structure of the atoms, i.e., the valence electrons, and the variations for one family are due to the difference of shells to which the valence electron belongs.

This feature of the periodic properties leads naturally to the assumption that any periodic property of the elements consists of two factors, the one is the periodic factor which determines the periodicity and the other the amplitude factor which causes the change of the properties of elements in the same family. Thus we may write:

$$P = A \cdot p \quad (1),$$

where  $P$  denotes a periodic property,  $p$  its periodicity factor which is a function of valence\*, and  $A$  its amplitude factor which is a function of energy state and the radius of the outermost shell.

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\* Besides the chemical properties, the so-called physical properties such as boiling point, melting point, surface tension, etc., are considered by Langmuir (19) as "manifestation of typical chemical forces, sometimes primary valence other times secondary valence forces."

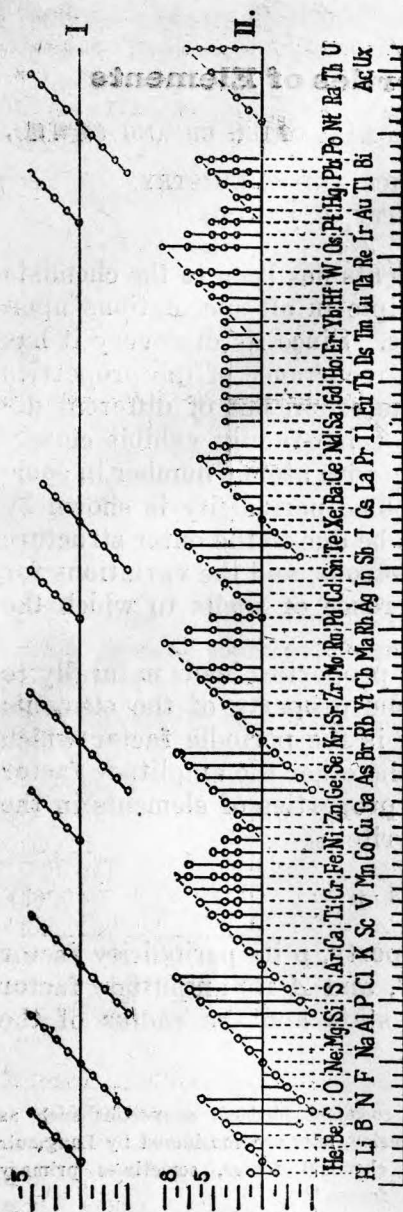


Fig. 1. Valence of elements: I. Abegg theory. II. After Langmuir (20).

## Periodicity Function

According to the periodic system the valence of the elements  $V$  is a periodic function of the atomic number,  $Z$ :

$$V = f(Z) \quad (2),$$

As assumed in the above paragraph:

$$p = \psi(V) \quad (3),$$

thus we have

$$p = \psi[f(Z)] \quad (4).$$

If we consider only the normal valence of the elements, without dealing with the mechanism of the valence bindings, it is sufficient to start with the Abegg theory, the rule of eight, as a basis for determining  $f(Z)$ .

Abegg's (1) rule states that every element can exhibit either positive or negative valence and the maximum positive valence is the same as the number of the periodic group to which the element belongs. The sum of the maximum positive and negative valences, irrespective of sign, is always equal to eight, as shown in the table below:

Periodic group	0	I	II	III	IV	V	VI	VII
Normal valence	0	1	2	3	$\pm 4$	-3	-2	-1
Contra-valence	(-7)	(-6)	(-5)		5	6	7	

Fig. 1 gives the curve of normal valence of Abegg's rule. For comparison, a diagram of

the kind first introduced by Kossel (17) and Langmuir (20), showing the possible valences of the known elements, is given in the same figure.

For the representation of the normal valence of the short periods as a function of the atomic number, we start with He as the origin and thus (Fig. 2):

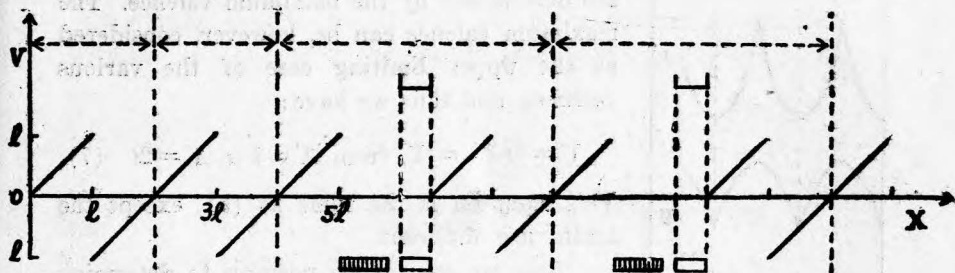


Fig. 2. Normal Valence of short and long Periods.

$$X = Z - A,$$

$$V = f(X) = X, \text{ from } X = 0 \text{ to } X = l \tag{5a},$$

$$V = f(X) = X - 2l, \text{ from } X = l \text{ to } X = 2l \tag{5b},$$

where  $l$  is the length of the period and  $A$  the atomic number of the inert gas before the period considered and is given by the Rydberg's atomic number series:

$$A = 2 (1 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 \dots) \tag{6}.$$

In the long periods the elements are always divided into two series of eight elements, A-series and B-series, and each series corresponds with a short period. The normal valence function (5) holds for the A-series. For B-series,  $A$  is replaced by the atomic number of the last member of each of the iron-platinum triads before the series considered, i.e.,  $A$  has the values 28, 46, and 78 for B-series of 4th, 5th, and 6th periods respectively.

Among the transition elements in the periodic system, those of the A-series of Groups V, VI, VII, and VIII are all exceptions to Abegg's rule. They have predominant contra-valences. In combination they play the parts of positive metallic ions and under oxidizing conditions they all increase in valence and form acids. Among them

we find the cases of multiple valences some of which are more stable than others, and the unstable ions readily change to others with other valences. For these elements the valence actually exhibited in special cases may be different not only from the normal valence, but also from the maximum one. It is not entirely correct in some cases

to assume that the properties of the elements are determined by the maximum valence. The maximum valence can be, however, considered as the upper limiting case of the various valences, and thus we have:

$$V = f(X) = X, \text{ from } X = l \text{ to } X = 2l \quad (7).$$

This equation is the same as (5), except the limits are different.

Now we are in the position to determine the relation between  $p$  and  $V$ . An exhaustive study of the type of all known periodic properties, with the exception of a minor class of few ionic properties, leads to the conclusion that nearly all the atomic periodic properties are of the "U"-shaped curves. Fig. 3 gives the typical types of the "U"-shaped curves for one period with the valence curve placed under these curves. The curves I, II, III and IV are of the possible types of the "U"-curves. The examples of I, II and III, are boiling point, density, and atomic volume respectively. There is no example of curve IV.

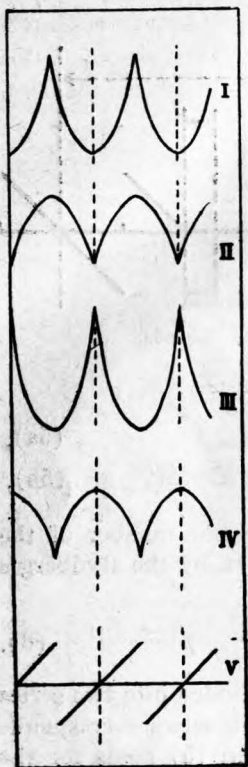


Fig 3 Typical Types of Periodicity of Properties.

From the above curves, it is observed that the periodic function  $p$  is of the parabolic type while the valence function is a broken straight line. This leads to the assumption that the periodic function  $p$  may be represented as an integral of the valence function:

$$p = \int V \, dZ \quad (8)$$

Substituting the function  $V$  in (8), we have:

$$p = \int X dX = \frac{1}{2} X^2 + c, \quad \text{from } X=0 \text{ to } X=l. \quad (9a),$$

$$p = \int (X-2l) dX = \frac{1}{2} (X-2l)^2 + c, \quad \text{from } X=l \text{ to } X=2l. \quad (9b).$$

For transition elements of groups V, VI, VII and VIII, the integration function of the maximum valence is the same as (9a) within the range from  $X=l$  to  $X=2l$ . Fig. (4) gives a curve of equation (9) with  $c=0$ . This is of the exactly same shape as curve I in Fig. 3.

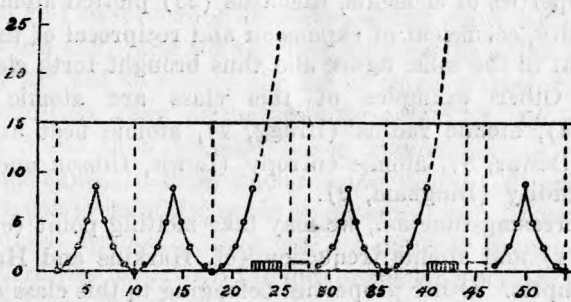


Fig. 4. Integral Function of Valence.

The other types of curves, II, III and IV, can also be represented by the same periodic factor, if we introduce an exponent  $\gamma$  for the function  $p$ . In general we may write.

$$P = A \cdot p^\gamma \\ = A \left[ \int v dz \right]^\gamma \quad (10)$$

If  $\gamma > 0$ , we have two cases:

- (1)  $\gamma > \frac{1}{2}$ ,  $p^\gamma$  gives curves of type I.
- (2)  $\gamma < \frac{1}{2}$ ,  $p^\gamma$  gives curves of type II or III, depending on the value of  $c$ .

If  $\gamma < 0$ ,  $p^\gamma$  gives curves of Type III or IV, depending on the value of  $c$ .\*

The difference between the types of periodicity is very significant. Types I and II have maximum at the center and minimum at both ends of a period, while types III and IV have minimum at the center

\* This may be easily proved by differentiating two times the function  $p$  as if it were a continuous one.

of a period and maximum at its both ends. For the sake of simplicity, we shall call both types I and II the increasing class and the types III and IV the decreasing class. These two classes are distinctly different from each other both in sign of  $\gamma$  and in the characteristics of curves.

The atomic volume curve, one of historical importance in the development of the periodic system, is a typical decreasing property. A number of other periodic properties later found exhibit an analogous behavior in the mode and characteristic. In his study on periodic properties of elements, Richards (25) plotted atomic volume, compressibility, coefficient of expansion and reciprocal of the absolute melting point in the same figure and thus brought forth clearly their analogues. Other examples of this class are atomic parachor (Sugden, 34), atomic radius (Bragg, 4), atomic heat at low temperatures (Dewar, 8), atomic entropy (Lewis, Gibson and Latimer, 21), and fluidity (Bingham, 2).

For increasing function, we may take melting point (cf. Harkins and Hall, 14) and atomic frequency (cf. Harkins and Hall, 14) as typical examples. Other properties belonging to this class are boiling point (Carnelley, 5), latent heat of fusion (Rudorf, 27), latent heat of vaporization (Washburn, 37), density (cf. Harkins and Hall, 14), hardness (cf. Rydberg, 28; and Harkins and Hall, 14) cohesion force  $Tm/v$  of Blom (3), intrinsic attraction (Tomlinson, 36), and atomic refraction (cf. Smiles, 33).

In the same class, either increasing or decreasing, the signs of  $\gamma$  for all the properties are the same and they have maxima and minima at corresponding positions and the curves seems to run parallel. This relationship is called by some previous investigators as parallelism. The relation between the latent heat of fusion and melting point as given by Trouton's rule is an example.

For an increasing function,  $\gamma > 0$ , while for a decreasing function,  $\gamma < 0$ . They are thus naturally reciprocal of each other:

$$\begin{aligned}
 P \text{ increasing} &= \left[ \int V dZ \right] \gamma \\
 P \text{ decreasing} &= \left[ \int V dZ \right] - [\gamma] = \frac{1}{P \text{ increasing}}. \quad (11)
 \end{aligned}$$

As a matter of fact, this reciprocal relationship had been noted

by some previous investigators. In 1913 Blom (3) gave curves for a number of oxides of the type  $RO$ , and showed that when the mean atomic heat, the square root of the atomic volume and softness (reciprocal of the hardness on Mohs scale) are plotted, as functions of the atomic weight, the three curves have the same form. In 1915, Richards (25) pointed out the reciprocal of absolute melting point, instead of the absolute melting point itself, is of the same type of the atomic volume. In the next year, Harkins and Hall (14) also plotted the four curves of atomic volume, compressibility, coefficient of expansion and reciprocal of absolute melting point for 72 elements as Richards did (25), and showed that all these have the same form, though they are not so closely similar as those plotted by Richards (25). In addition, they plotted the reciprocal of the atomic frequency and found that this also has a form similar to that of the atomic volume curve. In 1928, Richards and White (26) compared atomic volume, compressibility, cubic coefficient of expansion, reciprocal of absolute melting point, reciprocal of internal pressure, and reciprocal of hardness for IB-VB families of the long periods by plotting them in the same figure and emphasized the approximate proportionality between the atomic volume and the other properties plotted. All these conclusions cited above can be represented by the reciprocal relation as indicated in equation (11), since melting point, internal pressure, atomic frequency and hardness are increasing functions, and their reciprocals must be decreasing ones just like the typical decreasing property, atomic volume.

### **Amplitude function.**

Most of the amplitudes of the periodic properties of elements become either smaller and smaller, larger and larger, or smaller and larger alternately as the atomic number increases. In one family, the property curve with atomic number as abscissa is always a non-periodic one and either increases or decreases with an increase in atomic number. This is due to the fact that although the number of valence electrons of elements in the same family is the same, the energy states of these electrons which are determined by the quantum numbers and the atomic number, are different for different atoms in the same family. Electrons in different energy states are situated



in orbits of different radius and possess different energy values. The radius of the orbit and the energy values of the valence electrons contribute the variation of amplitude of the properties to the elements belonging to the same family.

A number of relationships between the atomic radius and the amplitude change of other properties had been pointed out by previous investigators. For the inert gases, the atomic radius,  $a = \frac{a^1 \cdot n^2}{z-s}$ , is found to be approximately proportional to the cubic root of atomic refraction, the cubic root of the van der Waals volume correction  $b$ , the square root of the van der Waals pressure correction  $a$ , the apparent atomic diameter  $\sigma$ , the boiling point, and the reciprocal of the ionization potential. Graphs of these properties, when plotted versus atomic radius as abscissa, are all straight lines (cf. Geiger and Scheel, 12). The cubic root of ionic refraction, normal potential, heat of hydration, reciprocal of the ionization potential, etc., for groups O, I, II, VI and VII have also been shown to be parallel with ionic radius (cf. Geiger and Scheel, 13).

Since both the energy and the radius of the orbit of the valence electron are function of atomic and quantum numbers, we may postulate that the amplitude function which represents both the variations caused by the change of radius of orbit and those by the energy state may be represented by the function:

$$A = k \frac{Z^{\alpha}}{n^{\beta}} \quad (12)$$

where  $k$  is a proportional constant,  $\alpha$  and  $\beta$  two parameters which are constants for elements of the same family and different for different families. For some properties the second quantum number  $l$ , or the resultant of  $l$ 's,  $L$ , may be introduced together with the principal quantum number. According to the signs and values of the exponents  $\alpha$  and  $\beta$ , various types of amplitudes may be represented by the amplitude function  $k \frac{Z^{\alpha}}{n^{\beta}}$ . In many cases, it, has been found that the amplitude function for one family is either one of the following three types: (1) concave upward increasing function, (2) concave downward increasing function, and (3) concave upward decreasing function. The example of the concave downward decreasing function

has not been found. Fig. 5 gives  $\frac{Z^{\frac{2}{3}}}{n}$ ,  $\frac{Z^{\frac{1}{2}}}{n}$  and  $\frac{Z^{-1}}{n^{-1}}$  of group IA as illustrations of the three types, the curves of atomic weight, atomic heat at low temperature, and atomic frequency of this group correspond with theoretical curves respectively.

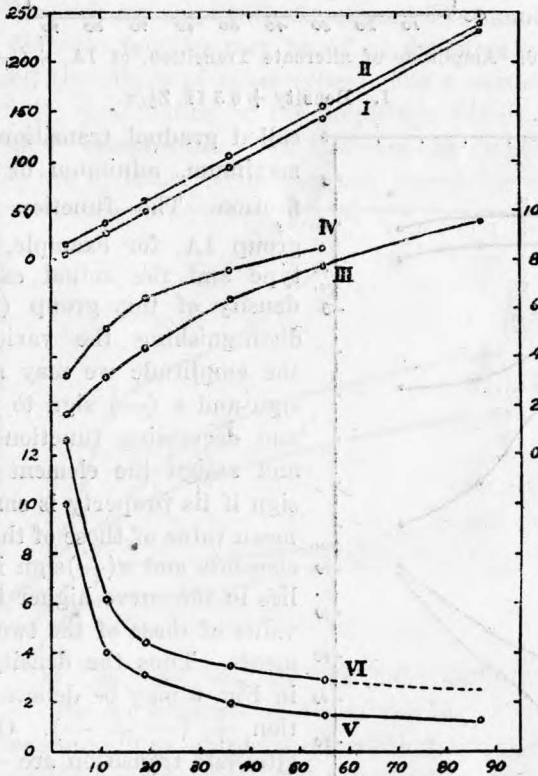


Fig. 5. Amplitude Functions of Group IA.

- |                                    |                                       |
|------------------------------------|---------------------------------------|
| I. $2 \frac{Z^{\frac{2}{3}}}{n}$ . | IV. At. Heat at low Temp. + 2.        |
| II. Atomic Weight + 10.            | V. $15 \frac{Z^{-1}}{n^{-1}}$ for IA. |
| III. $Z^{\frac{1}{2}}$ for IA.     | VI. Atomic Frequency.                 |

In most cases, the amplitude function  $k \frac{Z^a}{n^b}$ , does not give a curve which changes gradually from one element to the other, i.e., the so-

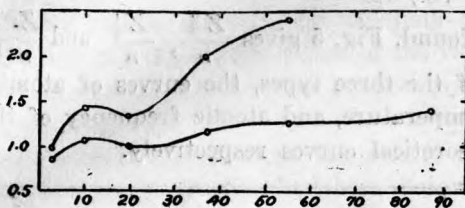


Fig. 6. Amplitude of alternate Transition. of IA, +(- + -)

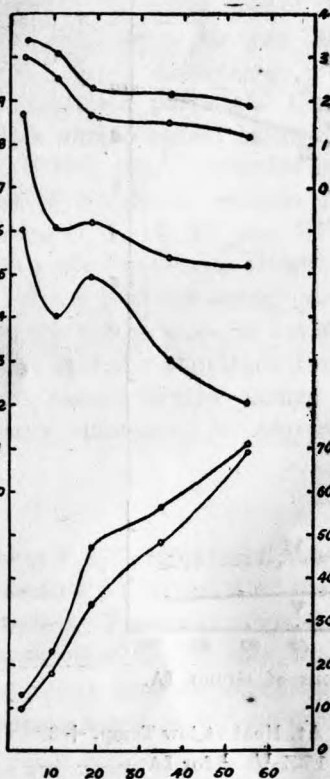
I. Density  $\dagger 0.5$  II.  $Z^{1/2}/n$ .

Fig. 7. Amplitude of alternate Transition of IA.

- I. Ionization Potential  $-2$ .
- II.  $Z^2/n^3$  III.  $10 \cdot z^{-1}/n^2$
- IV. Hardness  $\times 10$ .
- V. Atomic Vol. VI.  $2z^{-1}/n^3$ .

called gradual transition, but gives a maximum, minimum or point of inflection. The function  $A = \frac{Z^{1/2}}{n}$  for group IA, for example, is of such a type and the actual example is the density of this group (Fig. 6). For distinguishing the various types of the amplitude we may assign a (+) sign and a (-) sign to the increasing and decreasing functions respectively, and assign the element with a (+) sign if its property is smaller than the mean value of those of the two adjacent elements and a (-) sign if its property lies in the curve higher than the mean value of those of the two adjacent elements. Thus the density curve given in Fig. 6 may be denoted by the notation  $\dagger (- + -)$ . Other types of alternate transition are  $- (- + -)$ , the examples are  $\frac{z^2}{n^3}$  for group IA, and its first ionization potential;  $\dagger (+ - +)$ ,  $\frac{z^{-1}}{n^2}$  of Group IA and its atomic volume; and  $- (+ - +)$ ,  $\frac{z^{-1}}{n^2}$  for Group IA and its hardness. These properties are plotted in Fig 7.

The type  $(+ - +)$  and  $(- + -)$  are said to be of alternate transitions in contrast with the gradual transitions which are denoted by  $(+ + +)$  or  $(- - -)$ .

In the periodic system there are eight groups or sixteen families, and for each there is an amplitude function. The amplitude functions for the different families may be all of the same type or some of one type and the others of other types. For a certain property, there is a definite combination of the amplitude functions.

(1) "Parallel" combination. In this case the amplitudes of all the 16 families are of either simultaneously increasing or of simul-

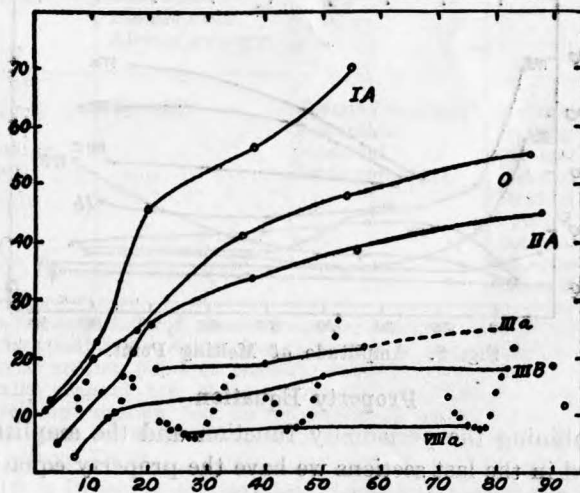


Fig. 8. Amplitude of Atomic Volume.

taneously decreasing. The amplitude variation of the bulk properties such as atomic radius, ionic radius, atomic volume and atomic parachor; their reciprocal properties such as density; and the ionization potential and ionic potential of Cartledge (7) are the examples. The fact that the bulk properties and their reciprocals belong to this type is easily understood. Since the radius of atoms of all groups increase with the atomic and quantum numbers, it is evident that if the amplitude of a property depends upon the size of the orbits of the valence electrons, all groups would change their amplitude in the same direction, either increasing or decreasing, and both the exponents  $\alpha$  and  $\beta$  are either positive or negative throughout

the whole periodic system. Fig. 8 gives the amplitude of the atomic volume.

(2) "Crossing" combination. In this case the amplitudes for electropositive and for electronegative groups vary just in the reverse order; if the one is increasing, the other is decreasing, and vice versa. The combination of increasing and decreasing functions gives a crossing change of the amplitude of the whole periodic system. The examples are melting point, boiling point, latent heat of fusion, latent heat of vaporization, hardness, etc. Fig. 9 gives the amplitude of the melting point.

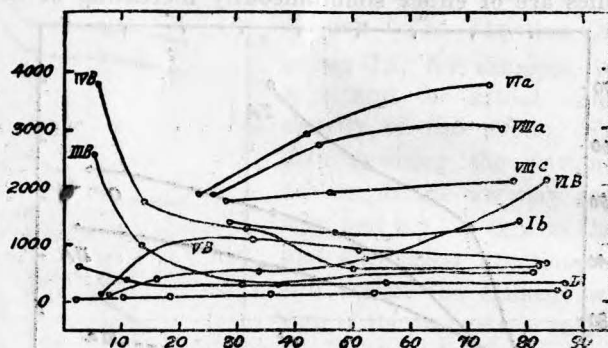


Fig. 8. Amplitude of Melting Point.

### Property Equation

By combining the periodicity function and the amplitude function obtained in the last sections we have the property equation:

$$P = k \frac{Z^a}{n^b} \left[ \int V dZ \right]^c \gamma \quad (13).$$

Since there are two types of amplitude, *i.e.*, parallel and crossing, and two classes of periodicity functions, *i.e.*, increasing and decreasing, we have the following types of periodic properties.

(1) **Parallel amplitude, increasing periodicity.** This is divided again into: (a) *increasing amplitude, increasing periodicity*, and (b) *decreasing amplitude, increasing periodicity*;

(2) **Parallel amplitude, decreasing periodicity.**

(3) **Crossing amplitude, increasing periodicity;**

(4) **Crossing amplitude, decreasing periodicity** (Table I).

In the case of parallel amplitude, decreasing periodicity we have

only properties of increasing amplitude; no example of decreasing amplitude has yet been found.

Table I.

Amplitude Properties Periodicity	Parallel Change		Crossing Change
	Increasing	Decreasing	
Decreasing ( $\gamma < 0$ )	Atomic Radius Atomic volume Atomic parachor Ionic radius Atomic heat Atomic entropy		Compressibility coefficient of expansion
Increasing ( $\gamma > 0$ )	Density	Atomic frequency† Ionization potential Ionic potential	Melting point Boiling point Critical temperature Heat of vaporization Heat of fusion Specific refraction Intrinsic pressure Hardness Cohesion*

† Though the amplitude of atomic frequency seems to be a parallel combination, it may be possibly a crossing change, since it is proportional to the square root of ratio of melting point (a crossing change) to two-thirds of atomic volume (a parallel change) (cf. Mellor, 22). The amplitudes of groups I-VIII are all decreasing function, but the amplitude of group 0 is increasing one.

\* Cohesion given by Harkins and Hall (14) is a ratio of melting point to the atomic volume  $T_m/\gamma$ .

In Fig. 10. a function of parallel increasing amplitude and decreasing periodicity  $P_{id}$ ;

$$P_{id} = k \frac{Z^a}{(n+L)^\beta} \left[ \int V dZ \right]^\gamma$$

where  $a = 0$ ,  $\beta = -1$ ,  $\gamma = -\frac{1}{2}$ ,  $k = 3$ , and integration constant  $c = \frac{1}{20}$ , is compared with the atomic volume<sup>(1)</sup> and atomic heat<sup>(2)</sup> at low temperature. Fig. 11 gives a comparison of a function of parallel increasing amplitude and increasing periodicity:

- (1) Data taken from Ephraim (9), except those for Ne, Ar, Kr, Xe, Em and Sc, which are calculated from atomic weight and density from the International Critical Tables (37).
- (2) Data for elements at 20-77.4° K., taken from Lewis and Randall (21a).

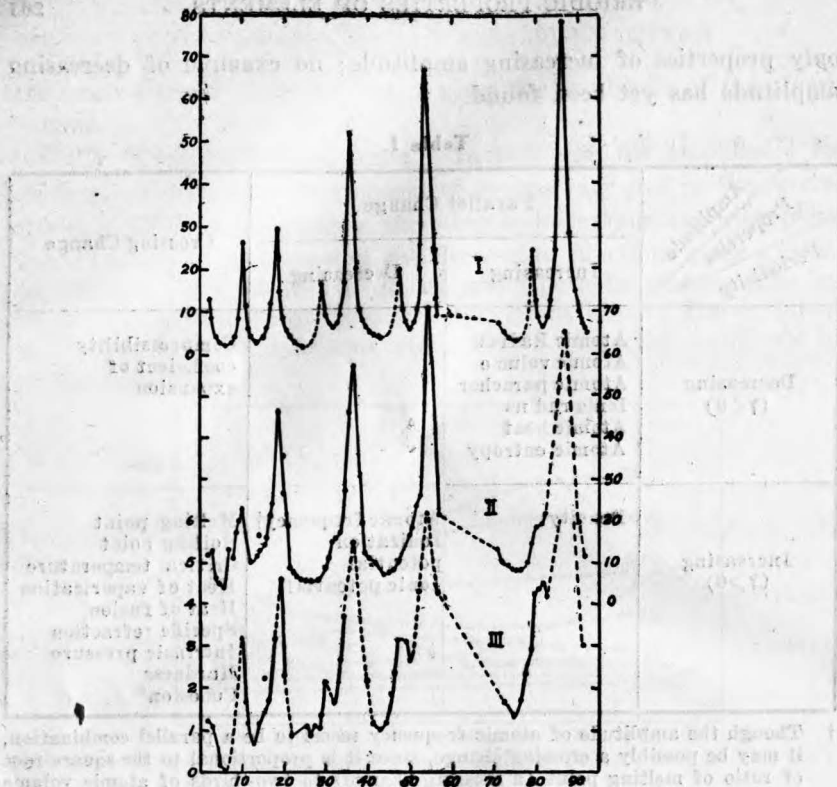


Fig. 10. I.  $3 \{Z^0/(n+L)^{-1}\} [\int \sqrt{V} dZ]^{-\frac{1}{2}}$ . II. Atomic Volume.  
 III. Atomic Heat at low Temperature.

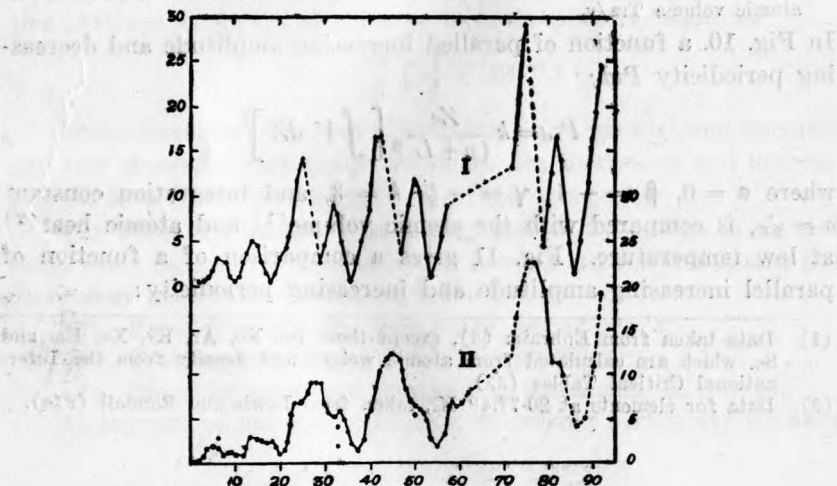


Fig. 10. I.  $(2/5) (Z^{5/6}/n^{\frac{1}{2}}) [\int \sqrt{V} dZ]^{-\frac{1}{2}}$ . II. Density

$$P_{ii} = k \frac{Z^a}{n^b} \left[ \int V dZ \right]^c,$$

where  $a = \frac{5}{8}$ ,  $b = \frac{1}{2}$ ,  $c = \frac{1}{2}$ ,  $k = \frac{2}{3}$  and  $c = \frac{1}{2\sigma}$ , with the curve of density<sup>(8)</sup>. Fig. 12, gives a comparison of a function of decreasing amplitude and increasing periodicity:

$$P_{di} = 50 \frac{Z^{-\frac{3}{2}}}{(n+L)^{-1}} \left[ \int V dZ \right]^{\frac{1}{2}},$$

with the atomic frequency<sup>(4)</sup> curve. Fig. 13 gives a function of crossing amplitude and increasing periodicity:

$$P_{ci} = A \left[ \int V dZ \right]$$

where  $A = 1800 \left(\frac{n}{Z}\right)$  for electropositive elements, and  $A = 18 \left(\frac{Z}{n}\right)$  for electronegative elements. In the same figure the melting point curve, boiling point<sup>(6)</sup> curve, and hardness<sup>(6)</sup> curve are plotted for comparison. In Fig. 14, a function of crossing amplitude and decreasing periodicity,  $[A \int V dZ]^{-\frac{1}{2}}$ , where  $A = 5 \frac{Z}{n}$  for groups IA-IVa,  $A = 60 \frac{Z^{\frac{1}{3}}}{n^2}$  for VB-VIIB and 0 and  $A = 100 \frac{n}{Z}$  for groups Va-VIIa and Ib-IVb, is compared with the compressibility<sup>(7)</sup>.

- 
- (3) Data taken from International Critical Tables (37).
  - (4) Data taken from Mellor (22).
  - (5) Data taken from International Critical Tables (37) and converted into absolute scale by adding 273° K.
  - (6) Data taken from Landolt-Börnstein (18).
  - (7) Data taken from Richards (24, 26).
  - (8) Data taken from Saha and Saha (29).



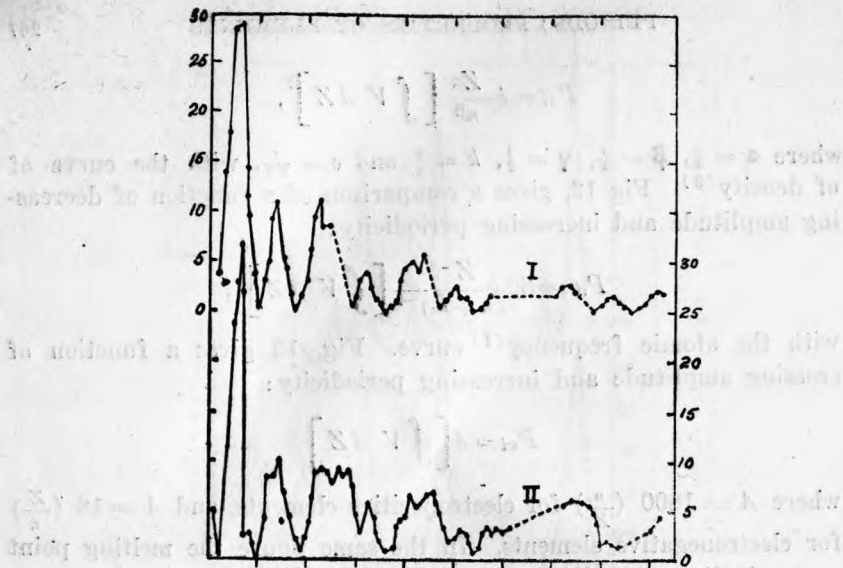


Fig. 12. I.  $50 \{Z^{-3/2}/(n+L)^{-1}\} [\int \sqrt{dZ}]_{\frac{1}{2}}$  II. Atomic Frequency.

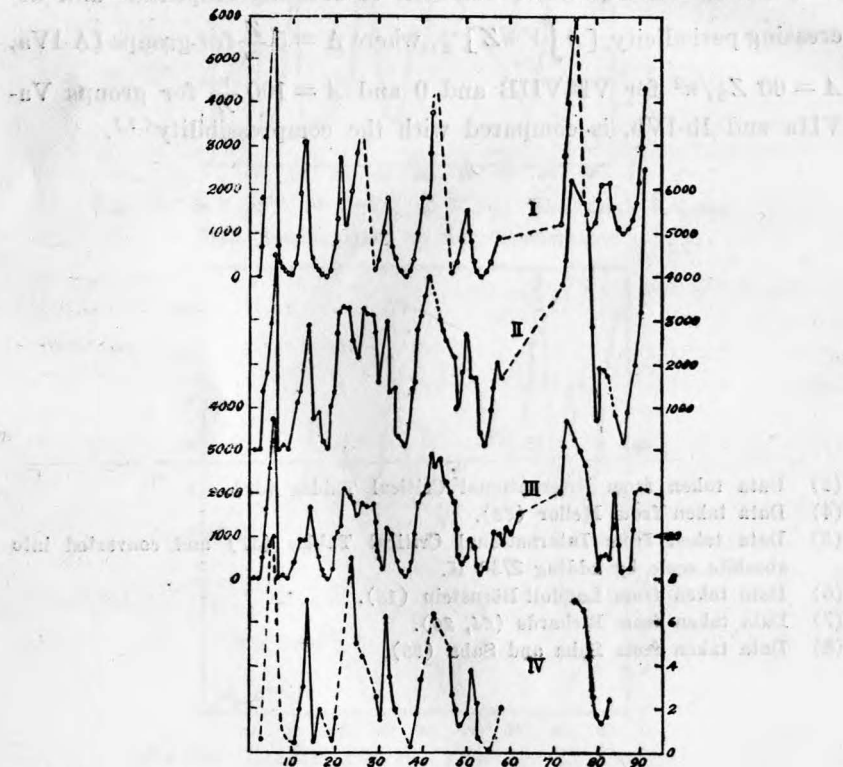


Fig. 13. I.  $A[\int \sqrt{dZ}]$ , II. Boiling Point. III. Melting Point. IV. Hardness.

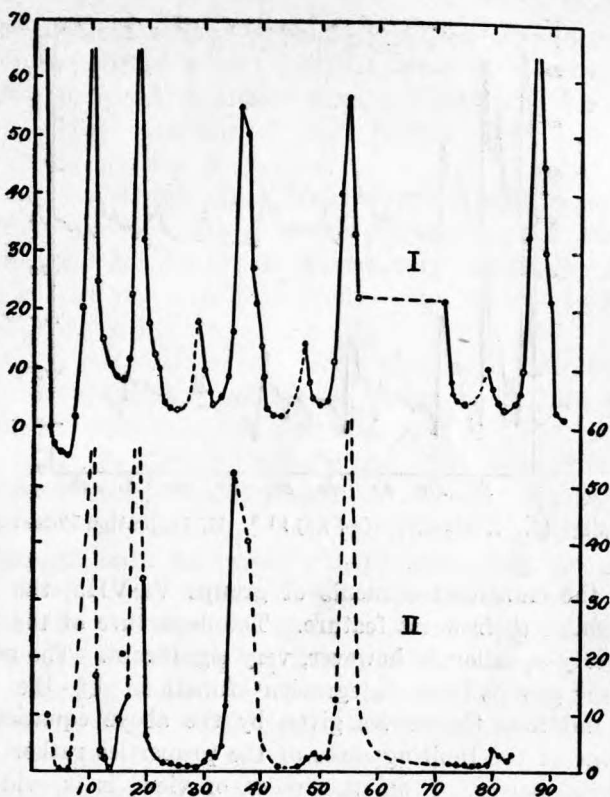


Fig. 14. I.  $A[V dZ]^{-\frac{1}{2}}$  II. Compressibility  $\times 10^6$ .

From the nature of its curve ionization potential seems directly related to the function of the number of valence electrons, but not determined by the valence itself. Its curve<sup>(8)</sup> (Fig. 15) very closely resembles the curve of the function:

$$13.5 \cdot \frac{Z^{\frac{1}{2}}}{n(n+L)} \cdot V^{\frac{1}{2}},$$

where  $V$  is the number of the valence electrons.

In these theoretical functions the values of the general constants  $\gamma$ ,  $k$ , and  $c$  and the family constants  $\alpha$  and  $\beta$  are all arbitrarily assigned and the curves give very characteristic resemblances for all the cases.

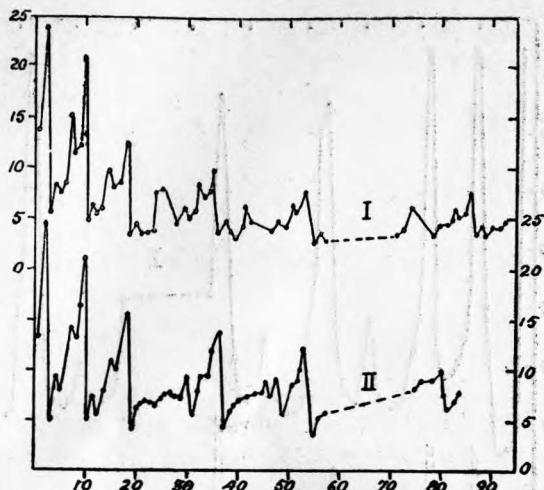


Fig. 15. I.  $13.5 \{Z^{\frac{1}{2}}/n(n+L)\} V^{1/2}$ , II. Ionization Potential.

For the transition elements of groups Va-VIIa, the theoretical curves exhibit their worst feature. The departure of the facts from the property equation is, however, very significant. The periodicities for these groups are integration functions of the maximum valence and thus the curves given by the above equations are the expressions of the limiting cases of the properties rather than those of facts themselves. From this point of view, it is evident that a theoretical curve should be an upper limit for an increasing periodicity property and a lower limit for a decreasing one. The actual curve for the former case should lie lower and that for the latter one higher than the theoretical curves. This is found to be so in most cases. It is found in the cases of increasing periodicity properties, *i.e.*, density, boiling point, melting point, atomic frequency and ionization potential, that the slope of the theoretical curve in the range of the transition groups Va-VIIa is always steeper than that of the corresponding portion of the actual curves.

## DISCUSSIONS

In the above property equation, we consider only the normal valence of the elements, the energy and the radius of the orbit

of the shells of the valence electrons, and then represent these in a form of a product of a periodicity function of valence  $V$  and an amplitude function  $A$  of atomic number  $Z$  and quantum number  $n$ . Besides these we have several other factors which may affect the feature of the periodic properties:

(1) *The allotropic effect.* Many elements exist in several forms which often possess quite different properties. For example, for carbon diamond has an atomic volume very low in the graph, but graphite has an atomic volume greater than that of beryllium and boron.

(2) *The molecular effect.* The molecules of different elements are made up of varying numbers of atoms, metals are monatomic, while sulfur is octatomic (cf. Ephraim, 10).

(3) *The condition of comparison.* Any comparison between elements must be made at corresponding states. No comparison can be made between liquid and non-liquid elements, as, for example, liquid nitrogen and solid carbon (cf. Ephraim, 10).

(4) *Interatomic forces.* Interatomic forces, such as polarization force, and van der Waals' force, are also responsible for the properties of the elements (cf. Slater and Frank, 32).

(5) *The mechanism of the valence.* The effect of valence linkage, electrovalence and covalence are sharply distinguished in volatility, solubility, electrical conductivity and many other properties (cf. Sidgwick, 31).

All these factors influence more or less the periodic properties of the elements. They are, however, not the determining factors of the main feature of the periodic properties.

In the recent studies of properties of elements, there is an increasing tendency to correlate the properties with the three fundamental quantities used in this paper, *i.e.*, atomic number, quantum number and valence. In 1928, Cartledge (6) first made an attempt to put the periodic system on a quantitative basis by introducing a function called ionic potential, a ratio of charge (valence) to radius of the ion. It has been observed that many chemical and physical properties of ions in the solid state and in solution can be correlated very well with this ratio. Two years later, Hume-Rothery (15, 16) found empirically that the interatomic distance is a function of the

principal quantum number of the outermost shell of the atomic core and the atomic number, with a constant coefficient  $a$  which in some groups may be connected with the valence:

$$\frac{d}{n} = \left( \frac{1}{aZ} \right)^x,$$

or

$$d = \left( \frac{1}{ax} \right) \frac{n}{Z^x},$$

where  $x$  is a constant for a group. This is called by Hume-Rothery the Law of Subgroup. The second relation he found was that for the ionization potential  $V$ , a linear relation exists between  $n^2 V$  and  $Z^{\frac{2}{3}}$  for the members of any one of groups, 0, IA and IIA, where  $n$  is the quantum number of the electron; thus we have:

$$V = k \frac{Z^{\frac{2}{3}}}{n^2}.$$

These relations are very similar to the property equation for a family. In 1935, Fersman (11) proposed the periodic system of the energy coefficient (a ratio of the square of valence to the radius of the ion), and the energy coefficient values of elements are considered to be in relation to the positions of elements in the periodic table, *i.e.*, atomic number. In the same year, Seith (30) found that the solubility of a metal in solid lead and the rate of diffusion of this metal in lead depends on its position in the periodic system (atomic number), on its atomic radius and on the number of the valence electrons. In 1936, Nekrasov (23) pointed out that the periodic table should show not only the resemblances of the elements in the neutral state, but also the resemblances and the differences in their ionic forms; and that the abrupt change in properties upon passing into a new ionic form is due to change in the charge, the radius of the atom and the structure of the outer shell. Most recently, in confirmation with Cartledge (16), Sun (35) found that the acidity of compounds of elements is determined by the ratio of valence and the ionic radius. From these investigations it is evident that the *atomic number*, *valence* and *quantum number* are the most important factors determining the main feature of most periodic properties.

## SUMMARY

A periodic property of the elements is represented by a property equation which consists of a periodicity factor and an amplitude factor in the form.

$$P = k \frac{Z^{\alpha}}{n^{\beta}} \left[ \int V dZ \right]^{\gamma},$$

where  $k$  and  $\gamma$  are general constants, and  $\alpha$  and  $\beta$  are family constants. The periodicity factor  $\left[ \int V dZ \right]^{\gamma}$ , an integral function of the valence, determines the periodicity of the properties; and the amplitude factor  $\frac{Z^{\alpha}}{n^{\beta}}$  which is determined by the energy and the radius of the orbit of the valence electrons, represents the variation of the amplitude of the property curve.

The combination of the two types of periodic functions, increasing ( $\gamma > 0$ ) and decreasing ( $\gamma < 0$ ), with the three types of amplitude functions, parallel increasing, parallel decreasing and crossing, gives all the known types of atomic properties. Curves of the property equation are compared with all the types of actual periodic property curves and very characteristic resemblances are found in all cases.

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